High-Temperature Pulsed-Field-Gradient ^7Li -NMR Measurements of Li_2CO_3 over 700 K

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Abstract

Understanding the transport property of Li ions is crucial for improving the performance of Li-ion batteries. To investigate the ion diffusion at high temperatures, we constructed a high-temperature pulsed-field-gradient (PFG) nuclear magnetic resonance (NMR) probe capable of measurements at temperatures >700 K. The accuracy of the sample temperature was confirmed via ^{79}Br NMR measurements of KBr. ^7Li PFG-NMR measurements of Li_2CO_3 were performed at temperatures up to 724 K using the probe. The apparent diffusion coefficient of Li ions in Li_2CO_3 was obtained experimentally.

Keywords: high temperature, pulsed field gradient, NMR, diffusion

Introduction

Understanding the transport property of Li ions is crucial for improving the performance of Li-ion batteries.¹ Among the many analytical methods, nuclear magnetic resonance (NMR) spectroscopy is one of the most important techniques for characterizing the local structure and Li-ion mobility from microscopic points of view. In particular, the Li-ion mobility in glass-ceramic ionic conductors has been investigated, as these conductors are potential solid electrolytes for all-solid-state batteries. The diffusion constant and the activation energy of the Li ions in glass-ceramic ion conductors were investigated using pulsed-field-gradient (PFG) NMR.²⁻⁴ However, PFG-NMR measurements of the battery materials were limited within the electrolytes owing to the low ion mobility and/or a short spin–spin relaxation time T_2 in cathode materials at room temperature. Most of the NMR studies on cathode materials focus on the local structures and electric properties.⁵ Few NMR studies have been performed on the Li-ion mobility in cathode materials.^{6,7} The Li-ion mobility is investigated through the spin–lattice relaxation time T_1 . The spin–lattice relaxation time T_1 shows minimum where the correlation time of the Li-ion mobility across the Larmor frequency. The activation energy of the ion mobility can be deduced from the temperature dependence of T_1 . However, the diffusion constant cannot be obtained from T_1 measurements. It is expected that the Li-ion diffusion measurement of Li-ion battery-related materials becomes possible at high temperatures. To investigate the ion diffusion at high temperatures, we constructed a high-temperature PFG-NMR probe capable of measurements at temperatures >700 K.

We performed ^7Li PFG NMR measurements of Li_2CO_3 at temperatures up to 724 K using the newly constructed probe. Li_2CO_3 is extensively studied as a component of the solid–electrolyte interphase (SEI) of Li-ion batteries. The SEI is formed on both the

anode and cathode surfaces, which affects the battery performance. The ion diffusivity of Li_2CO_3 has been studied only through numerical calculations.⁸⁻¹⁰ To the best of our knowledge, this study is the first experimental report on the Li-ion diffusion of Li_2CO_3 .

Experimental

We constructed a high-temperature PFG-NMR probe in collaboration with an instrument company JEOL and integrated it into a 500 MHz NMR system (ECA500) with a wide-bore superconducting magnet operating at 11.7 T. The probe was equipped with a double-resonance circuit for ^1H as a high-frequency nucleus and for multinuclear systems including ^2D , ^{13}C , and ^7Li as low-frequency nuclei. A similar high-temperature PFG-NMR probe for a 500 MHz system was previously developed.¹¹ The electric circuit for radio frequency signal and PFG in this study is almost the same with that reported in Ref. 11, because the previous probe was also developed in collaboration with the same company JEOL. However, the previous probe was intended for PFG-NMR measurements of hot water, e.g., in the supercritical condition. Thus, a special sample tube and a ceramic sample holder must be used to reduce the amount of damage to the probe assembly in the case of the explosion of hot water at a high pressure. In this study, we constructed a probe with a standard NMR sample tube having a diameter of 5 mm. Using the standard sample tube facilitated the preparation of the sample, and the signal-to-noise ratio was improved owing to the large sample volume.

The temperature of the sample was varied from 296 K to 724 K by a flow of heated nitrogen gas. The temperature of the nitrogen gas was monitored by a thermocouple and changed by a heater located below the sample tube. The sample temperature was calibrated by recording the temperature measured by a thermocouple tentatively located

at the sample position while increasing the gas temperature. The accuracy of the temperature calibration was confirmed by the ^{79}Br NMR measurements of KBr. The ^{79}Br NMR spectrum was obtained with a single pulse sequence. The spin–lattice relaxation time T_1 was measured via a saturation recovery method.

The powder sample of Li_2CO_3 was purchased from Kanto Chemical, Co., Ltd. The sample was inserted in a sample tube made of quartz, SS-002 (Shigemi, Tokyo, Japan) with a height of 5 mm. The ^7Li NMR spectrum was obtained with a single pulse sequence. The tuning and the matching of the probe was adjusted at each temperature. The excitation radiofrequency pulse width was kept 25 μs at all temperature. The Li-ion diffusion was observed by the stimulated echo (STE) PFG sequence.¹² The PFG was generated with a current source up 30 A controlled by the spectrometer. In the STE-PFG NMR measurements, the echo amplitude E was related to the strength of the field gradient g , duration δ of the PFG, and time interval Δ of two PFGs. The diffusion constant D can be calculated using the Stejskal and Tanner equation:^{12,13}

$$E = E_0 \exp\left(-\gamma^2 \delta^2 g^2 D \left(\Delta - \frac{\delta}{3}\right)\right) = E_0 \exp(-bD) , \quad (1)$$

where γ represents the ^7Li gyromagnetic ratio ($1.039 \times 10^8 \text{ s}^{-1}\text{T}^{-1}$). The echo attenuation was observed by varying g from 0.13 to 1.32 T/m with $\delta = 1 \text{ ms}$ and $\Delta = 1.5 \text{ ms}$. The strength g was calibrated so that the diffusion constant of Li ions in aqueous LiCl (1 mol dm^{-3}) at room temperature was $0.9 \times 10^{-9} \text{ m}^2\text{s}^{-1}$.¹⁴

Results and Discussion

First, the accuracy of the sample temperature was confirmed by ^{79}Br NMR measurements of KBr. The spin–lattice relaxation time T_1 and chemical shift were measured in the temperature range of 298–700 K. T_1 decreased with increasing temperature (Figure 1).

The temperature dependence of T_1 in KBr is explained by the quadrupolar relaxation process in the temperature range of 20–296 K.¹⁵ Above the Debye temperature Θ_D , the temperature dependence of T_1^{-1} due to the first-order Raman process in KBr is given by

$$T_1^{-1} = A \left(\frac{T}{\Theta_D} \right)^2 \left(1 - 0.056 \left(\frac{T}{\Theta_D} \right)^{-2} \right), \quad (2)$$

where A is an adjustable parameter for overall normalization.¹⁶ The temperature dependence of T_1 in this study is well explained by the theoretical value calculated by Eq. (2) with $\Theta_D = 177$ K and $A = 5.11 \text{ s}^{-1}$ (solid line in Figure 1). The good agreement between the experimental and theoretical T_1 values indicates the high accuracy of the sample temperature. The sample temperature was also confirmed by the chemical shift of ^{79}Br . The chemical shift was determined in the accuracy of ± 0.5 ppm by fitting the spectrum with the Voigt function. The chemical shift decreased with increasing temperature (Figure 2). A linear fit yielded a slope of -0.0301 ± 0.0003 ppm/K (solid line in Figure 2). The temperature dependence of the chemical shift of ^{79}Br was reported to be -0.0249 ± 0.0015 ppm/K in the temperature range of 260–324 K.¹⁵ The difference in the coefficient values may have arisen from the difference in the temperature. When we adopted the previously reported value for the change in the chemical shift at the high temperatures of this study, the nominal sample temperature exceeded the temperature of the heated nitrogen gas. This situation should not have occurred, because the thermocouple for the nitrogen gas was placed between the heater and the sample. Thus, it appears that the coefficient value of this study is valid for high-temperature measurements.

The ^7Li NMR spectrum of Li_2CO_3 was measured in the temperature range of 296–724 K (Figure 3). A broad peak began to narrow above 450 K, where the Li-ion motion started to average the ^7Li homonuclear dipole interaction. This behavior is consistent with the results of Dunstan *et al.*⁹ The full line-width at half height of the spectrum was almost constant above 660 K. The STE-PFG NMR measurements were

performed in the temperature range of 660–724 K. The STE signal was not observed below 660 K because the spin–spin relaxation time T_2 was shorter than the PFG duration δ . The ^7Li echo amplitude decreased with increasing the amplitude g of the PFG (Figure 4 for 724 K). The apparent diffusion constant D_{apparent} was obtained by fitting the data with Eq. (1). The apparent diffusion constant was almost constant and decreased slightly with the increasing temperature (Figure 5). This was unexpected, as the diffusion constant was expected to obey the Arrhenius law, where the diffusion constant increases with the temperature.⁴ Furthermore, the apparent diffusion constant is too large for a conventional Li-ion diffusion constant in solids.^{2–4} Thus, it seems that these results do not represent the conventional diffusion constant. It is reported that the apparent diffusion constants of powder Li-ion conductors depend on the diffusion time Δ .^{17–19} The D_{apparent} values become smaller as Δ become longer and approach an equilibrated small value. The Arrhenius behavior was observed for the smallest D_{apparent} which was obtained with a large Δ .^{17–18} In this study, a short $\Delta = 1.5$ ms was adapted to observe the STE signal with a short T_2 , resulting in a large D_{apparent} . The origin of the large D_{apparent} obtained with a short Δ is ascribed to grain boundaries, though the detailed mechanism is not clear.^{18–19} The ion migration influenced by grain boundaries is reported to be insensitive to temperature.¹⁹ It seems that the observed anomalous behavior of the D_{apparent} of powder Li_2CO_3 in this study is also ascribed to grain boundaries. It is reported that the anomalous behavior of the D_{apparent} is reduced for a single crystal.¹⁸ The spin-spin relaxation time T_2 of a single crystal is reported to be longer than that in a powder sample. The PFG-NMR measurement of single crystal Li_2CO_3 is desired to investigate the effect of grain boundaries on the Li-ion migration and remains as further work.

In summary, we successfully measured the apparent diffusion constant of Li ions in powder Li_2CO_3 at high temperatures for the first time via the PFG-NMR method

with a newly constructed probe. An unexpected behavior of the apparent diffusion constant at high temperatures was observed and ascribed to the effect of the grain boundaries. The results of this study indicate that PFG-NMR measurements at high temperatures are useful to investigate the ion migration in Li-ion battery-related materials.

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Figure Captions

Fig. 1 ^{79}Br spin–lattice relaxation time T_1 of KBr as a function of the temperature. The solid line is a theoretical curve for the quadrupole relaxation due to phonons.

Fig. 2 ^{79}Br chemical shift of KBr as a function of the temperature. The solid line is a linear fit. The chemical shift is normalized to 0 ppm at 298 K.

Fig. 3 Temperature dependence of ^7Li NMR spectra of Li_2CO_3 .

Fig. 4 ^7Li echo attenuation plot obeying the Stejskal and Tanner equation for Li_2CO_3 at 724 K.

Fig. 5 ^7Li diffusion constant as a function of the inverse temperature for Li_2CO_3 .

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

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